



# In-Situ Chemical Oxidation

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## **Notice**

The Technology Evaluation Group (TEG) completed this evaluation of In-Situ Chemical Oxidation based on professional expertise and review of items listed in the “References” section of this document. The criteria for performing the evaluation are generally described in the IDEM OLQ technical memorandum, *Submittal Guidance for Evaluation of Remediation Technologies*.

This evaluation does not approve this technology nor does it verify its effectiveness in conditions not identified here. Mention of trade names or commercial products does not constitute endorsement or recommendation by the IDEM for use.

## **Background**

Chemical Oxidation of contaminants involves injecting or emplacing a highly reactive substance to break apart the bonds in a contaminant compound, usually by inserting oxygen. It will physically destroy the molecule. This is notably different from bioremediation, in which microbes gradually strip off elements for use as food, but leave the rest of the molecule intact.

There are numerous types of in-situ chemical oxidation (ISCO) systems. The Office of Land Quality has evaluated various remediation applications using hydrogen peroxide (Fenton’s Reagent – a peroxide/iron catalyst mixture), magnesium peroxide, magnesium hydroxide, ozone, calcium peroxide, and sodium persulfate; with or without special catalysts, pH adjustment compounds, and iron supplements. All of these are intended to chemically break down contamination. Some of these have oxygen as a theoretical end product, which may stimulate aerobic microbes (those not killed by the peroxides and toxic secondary chemicals).

These chemical oxidants should not be confused with agents such as Oxygen Release Compound (ORC)<sup>™</sup> sold by Regenesis, which is a magnesium peroxide with phosphate added to form time-release crystals. ORC is used to provide oxygen to stimulate microbial action, rather than for chemical oxidation (see Office of Land Quality technical memo on ORC<sup>™</sup> applications).

## **Types of In-Situ Chemical Oxidation**

- Hydrogen Peroxide or Fenton's Reaction/Reagent. Fenton's Reaction requires acidic conditions (pH between 2.5 and 3.5), which are difficult to create in-situ, particularly in Indiana's carbonate rich soils and limestone areas. (Typical pH in Indiana's glacial soils is near 8.) The USEPA (2004, page XIII-5) states, "Because of the low pH requirement, Fenton's Reagent treatment may not be efficient or effective in limestone geology or sediments with elevated pH levels, or with significant capacity to buffer these reactions." With the above problems, "A classical Fenton's system cannot be readily created in situ as it is generally too difficult to maintain a well-mixed, low-peroxide concentration in the subsurface" (ITRC 2005, page 11). Under ideal conditions, peroxides can degrade TCA, PCE, TCE, DCE, VC, BTEX, phenols, MTBE, and explosives. It works poorly on DCA, PAHs, and PCBs; and almost not at all on pesticides. There are notable safety problems with the use of peroxides (see below).
- "Modified", or "non pH dependant, Fenton's Reaction." These systems do not actually produce Fenton's Reaction, but capitalize on the name. There are two general types of "modified Fenton's" systems. One uses hydrogen peroxide and a chelating agent or "special formula" to keep the iron catalyst available without acidic conditions. The other type of "modified Fenton's" uses calcium or magnesium peroxide to provide a slower-release hydrogen peroxide. "This type of system is significantly more complicated than traditional Fenton's" (ITRC 2005, page 11), and can be even more difficult to sustain. The solid peroxide compounds (magnesium peroxide and calcium peroxide, which are mixed with water for application) produce similar effects to liquid hydrogen peroxide, but at a slower rate, taking up to several weeks to attenuate. This provides a slower and safer exothermic reaction than the liquid hydrogen peroxide, but the same precautions are still needed for their use. The slower reaction would also hopefully allow for more time for the compound to be distributed in the subsurface. However, like hydrogen peroxide, they are more effective oxidizers at lower pH ranges.
- Permanganates. This is used in the form of potassium permanganate or sodium permanganate. Both degrade far slower than the peroxides, and can be emplaced easier. Permanganates can be used under a wide range of pH conditions, and do not produce the heat, steam, and vapors often produced by the peroxides. There are still some significant safety/explosive issues (see below). Permanganate can work well with PCE, TCE, DCE, VC, PAHs, phenols, and explosives. It is a poor degrader of benzene, pesticides, TCA, and PCBs.
- Ozone. Since ozone is a gas, it can be emplaced by injection into the vadose zone, by ozone sparging, or by injection of ozonated water. Ozone is highly reactive, but has a short half life (roughly 20 minutes) and needs to be generated close to the treatment area. Unlike other chemical oxidation techniques, ozone injection requires a semi-permanent remediation system. Corrosion resistant piping and injection points will be needed. Injection wells or sparge points need to be placed closely together. Fugitive ozone emissions during production or

injection may represent unacceptable risks, and a vapor collection system may be necessary (Huling and Pivetz, 2006). Ozone is capable of degrading PCE, TCE, DCE, VC, BTEX, phenols, MTBE, TBA, and explosives. It reacts poorly with DCA, PAHs, TCA, PCBs, and pesticides.

- **Persulfates.** Sodium persulfate is the only persulfate compound applicable for environmental applications (Huling and Pivetz, 2006). The oxidative strength of persulfates changes drastically with variations in pH, temperature, and the presence of ferrous ions. Persulfates usually require the presence of an activator, usually chelated (reduced) iron, which must be emplaced along with the persulfate, not mixed before injection. Other activators are heat and ultraviolet light. The balance of a chemical activator to persulfate is difficult to achieve in the subsurface because the two compounds differ in their transport behavior upon injection (Huling and Pivetz, 2006). Under ideal conditions, activated persulfates can degrade PCE, TCE, DCE, VC, BTEX, phenols, MTBE, and TBA. They are a poor degrader of PAHs, explosives, pesticides, and PCBs.
- **RegenOx™.** This is a product from Regenesis, the makers of ORC. RegenOx is a proprietary sodium percarbonate blend which is catalyzed to slowly release oxidant over approximately 30 days. RegenOx operates under alkaline conditions, and, unlike hydrogen peroxide and persulfates, does not require the manipulation of subsurface geochemistry. Regenesis proposes this technology as a prelude to or concurrent with enhanced bioremediation. According to the manufacturer, RegenOx is an effective oxidizer of nearly all common contaminants (Regenesis, 2007, page 16), but this has not been independently verified.
- **Zero Valent Iron.** Although this is sometimes listed as an ISCO, zero valent iron removes contaminants via reduction rather than oxidation. This is a completely different set of reactions and geochemistry, and is discussed at length in a separate Science Services technical memo.

Several of the above oxidative materials are often combined, such as ozone and peroxides. These combinations may work better than one compound alone, but most have the same advantages and disadvantages of the original compounds. Combinations of varied proportions of the above components are often issued under a trade name. Mixtures of peroxides and sodium percarbonate, and mixtures of persulfates (without activators) and peroxides are being sold by vendors. Some of these ISCO mixes may be a problem in that the amount of any one compound delivered may be too dilute to have much effect, particularly in low permeable soils.

### **Advantages**

- Chemical oxidation is usually much faster (weeks or months) than most other remediation methods.
- With the exception of off-gassing from hydrogen peroxide and ozone use, ISCO does not leave wastes to treat or transport.

- Oxidization destroys the molecules of contaminant, so there are not more toxic breakdown products, as may be the case in bioremediation.
- Oxidation enhances the mass transfer (desorption) of contaminants into vapor and dissolved phases, where they can be more easily captured or treated in-situ.
- Chemical oxidation can also be applied to plumes of mixed contaminants (such as petroleum mixed with solvents) that are not easily remediated in-situ with compatible technologies.
- Some ISCO applications are less invasive and cause less site disruption than other remediation methods.
- Some oxidants produce oxygen, which will help aerobic microbial decomposition of some hydrocarbons.
- Chemical oxidation may be cost-effective, particularly compared to engineered systems.

### **Limitations**

- There are notable health and safety issues involved with the handling and application of strong oxidizers. Permanganates are hazardous to handle ex-situ, and hydrogen peroxide has a violently exothermic reaction to free product.
- Chemical oxidation enhances mass transfer (desorption) of contaminants into vapor and dissolved phases. This may allow contaminant mobilization outside the monitoring area.
- Groundwater contaminant levels often rebound, and multiple injection events are necessary.
- It is difficult to deliver oxidant into areas having heterogeneous geology. It is nearly impossible to deliver oxidant into low permeability units.
- Oxidants tend to react quickly, which greatly limits their radius of influence beyond the injection point. Closely spaced, low volume injection points are usually best.
- The high natural oxidant demand in many Indiana soils means that there are many non-target compounds competing for the oxidant. Extremely large volumes of oxidant may be needed to achieve meaningful results.
- ISCO rarely remediates the entire contaminant mass; residual contaminants typically need additional treatment, monitoring and/or risk assessment.
- It is not economically viable to remediate large areas of NAPL.

- The manganese from permanganates and the iron catalysts used for Fenton's Reaction and persulfate precipitate out in the formation and cause notable reductions in permeability.
- Metals can be mobilized by changes in their oxidation state.
- Additional monitoring and safety requirements may make ISCO cost prohibitive compared to other active remedies.

### **Primary Issues When Considering ISCO for Sites in Indiana**

- Site Characterization. Once oxidants are injected into the subsurface, it is not easy to determine where they will go nor control how they will react. Thus, sites which propose chemical oxidation as a part of their remedy need to have a more in-depth examination of the subsurface conditions than is typical for sites choosing extraction or biodegradation. The contamination always needs to be fully delineated and the geology completely characterized BEFORE injections of substrate begin.
  - The investigation should include precise delineation of free product. NAPL can cause violent exothermic reactions with peroxides. Other chemical oxidation techniques require NAPL delineation to correctly calculate the amount and density of injections and prevent remedy failure.
  - All utility lines, possible migration pathways such as piping, and subsurface heterogeneities need to be explicitly mapped. These preferential pathways can allow desorbed contaminants to move in unexpected directions and prevent oxidant from reaching the contaminant mass.
  - An assessment of the soil and groundwater properties, plus the geochemistry is vital. The contractor must be able to predict how the natural environment will react to the oxidant prior to selecting a chemical oxidation strategy. Tests which need to be completed for remedial design include:
    - Site specific hydraulic conductivity, soil permeability, soil porosity, and particle size distribution. These values should not be estimated from a book value. Slug tests are acceptable only for screening and not remedial design.
    - Natural oxidant demand (NOD) of the soil and groundwater. The NOD will show the other compounds in the subsurface which will compete with the contaminant to be oxidized.
    - Field water quality parameters such as pH, dissolved oxygen, dissolved carbon dioxide, temperature, specific conductance, and oxidation-reduction potential

- Contaminant Mobilization

- Desorption. Even if the oxidants are effective on the contaminants, there may be other effects. The ITRC (2005, page 18) notes “However, because of the reactivity of the oxidants, there is the potential to cause a significant change in both the concentration and distribution of contamination, potentially resulting in large changes in a site’s established equilibrium of contaminants between the vapor, liquid, and sorbed phases.” In other words, the contaminants may be mobilized. There may be an increase in vapors, or redistribution of contamination from the sorbed phase into groundwater. The results of trial applications of solid and liquid peroxides at different sites in Indiana have all shown an increase in hydrocarbon concentrations in groundwater after application, due to the desorption effect from the oxidants, that tends to mobilize adsorbed hydrocarbons rather than chemically break them down.
- Flushing. A major consideration in all liquid ISCO applications is the amount of fluid introduced during the oxidant emplacement, particularly in the source area. The same volume of fluid will be displaced as is introduced. This can spread contamination further. Also it can cause a misleading impression that the oxidant is reducing contamination, when only dilution or dispersion is taking place. An extensive monitoring system is needed to warn against an expansion of the contaminant plume.

A poorly planned ISCO system may lead to a much larger contaminant plume than existed before application. Because of this, the contaminant plume must be completely and tightly delineated prior to injection. A contingency plan must be in place which details the response to adverse contaminant mobilization. Also, desorption and flushing can be used advantageously as a treatment for a recalcitrant source or inaccessible area of the plume. The mobilized contaminant can be captured or treated in-situ, down-gradient.

- Metals Mobilization. “In all ISCO projects it is important to know what metals are present in the soil and groundwater because this treatment technology can oxidize some metals, including iron, chromium, and selenium, to a more soluble form, thereby increasing their migration potential...Knowing which metals are present will aid in the selection of metals that should be monitored throughout the injection. The initial investigation should include the following metals at a minimum: arsenic, barium, cadmium, copper, iron, lead, and selenium” (ITRC 2005, page 24).
- Costs. Because of the necessary monitoring and safety precautions, chemical oxidation may have “potentially higher initial and overall costs relative to other source area solutions” (USEPA 2004, page XIII-3). Most of the safety precautions and monitoring that the USEPA states are needed, and the ITRC advises, have not been included on Indiana sites. For public safety, they need to be considered.

## **Oxidant Distribution Considerations**

- The most serious problem in using ISCO in Indiana is getting enough oxidant in contact with the contamination. “Chemical oxidants may not be able to penetrate low permeability homogeneous soils or horizons in heterogeneous soils that contain the bulk of petroleum contaminant mass” (USEPA 2004, page XIII-2). Most tills are too tight for effective oxidant emplacement. Inhomogeneous layers are also difficult, as the injected oxidants will follow the most permeable layer, and little will penetrate the tighter material. “In addition, the tendency for the development or enhancement of preferential flow paths may be increased by the addition of Fenton’s reagent or the use of ozone sparging” (USEPA 2004, page XIII-22). “Typical ROIs (radius of influence) for injections range from 2.5 feet for tight clays to 25 feet in permeable saturated soils” (ITRC 2005, page 48).
- Another problem that occurs when attempting to determine the ROI for planning injection spacing is that “Oxidant transport can be reaction limited because the oxidants are being depleted as they move through the subsurface. Therefore, the effective radius of oxidation treatment may be substantially less than the hydraulic (or pneumatic in the case of ozone gas) ROI” (ITRC 2005, page 46). The depletion of oxidants is due to the presence of compounds that raise the natural oxidant demand (NOD). These compounds are naturally occurring organic or inorganic substances that have a greater oxidant demand than most contaminants, so will react with the oxidants first, leaving less for remediation. Organic matter or humic acids have very large oxidant demands. Peat layers generally prohibit use of oxidants. Inorganic oxidant demands come from nitrification and the oxidation of sulfide, iron, iron sulfide, chromium, selenium, manganese, etc. “NOD almost always exceeds contaminant oxygen demand” (USEPA 2004, page XIII-19). In many cases, the amount of oxidants injected is too small to overcome the NOD and attack the contamination. Too much oxidant can cause excessive mineralization, death of local microbial populations, and reduced efficiency. Therefore, the NOD must be known before a corrective action plan (CAP) using oxidants can be prepared. “The results of laboratory-scale testing of an ISCO technology may or may not be directly (linearly) applied to the design of a corresponding pilot-scale study...Nonetheless, laboratory-scale tests are essential for estimating site-specific oxidant demand due to the soil matrix” (ITRC 2005, pages 40-41). Additionally, how bench-scale oxidant demand values relate to field oxidant demand has not been quantitatively established (Huling and Pivetz, 2006).
- In addition to the difficulty of penetrating low permeable formations, oxidants often form metal precipitates (usually iron or manganese oxides) that can further clog pore spaces, and reduce the ROI. “An important side reaction also occurs resulting in the formation of precipitates---it involves the reaction of two end products of this chain reaction, hydroxide ions and  $Fe(III)$ ” to form an “amorphous iron oxide (precipitate). This side reaction consumes available iron and is favored by a basic pH” (ITRC 2005, page 11). Manganese oxide is particularly deposited by permanganate injections.

- Solid compounds used for ISCO are usually mixed into a slurry and injected. Some of the injection methods require the compounds to be diluted to 10% or less, which greatly reduces effectiveness (see Office of Land Quality technical memo on the Direct Injection Device (DID) system). At that dilution, it is difficult to inject enough of the active ingredients into low permeable soils to produce the desired cleanup. Also, all oxidants will react with water, and the act of producing a slurry will start oxidant depletion, the rate of which depends on the oxidant compound and amount of water.
- Another point to consider is that the injection of large amounts of water into a contaminated area will dilute the amount of contamination present. “An issue that must be resolved when assessing treatment effectiveness is the role of displacement of contaminated water away from the injection points. Depending on sampling locations observed, post-injection declines might reflect the displacement of contaminated water rather than actual contaminant mass destruction” (ITRC 2005, page 56). Any area where oxidants are injected needs to have a comprehensive monitoring well system in place. Monitoring should start before oxidant injection, and continue at least a year after (see above). Transducers are the best way to monitor water levels over time.
- “ISCO is an aqueous-phase technology, so except for ozone, the oxidant must be applied to a [sic] saturated or near saturated conditions” (ITRC 2005, page 21). Application of chemical oxidants to soil contamination has resulted in a much larger contaminated area than before injection, (see above). By their nature, chemical oxidation treatments are applicable to the saturated zone only.

## **Monitoring**

- Oxidant remediation is not an easy to assess, one time application strategy. Both the USEPA (2004, page XIII-45), and the ITRC (2005, page 60), call for monitoring of oxidant remediation sites for a minimum of one year after injection, to guard against rebound. According to Regenesis (2007), 88% of sites using chemical oxidation had contaminant rebound in at least one well.
- There is also additional monitoring needed during the remediation process, as mentioned above. Huling and Pivetz (2006) recommends process monitoring of all ISCO applications for:
  - Oxidants,
  - Metals,
  - Iron, phosphates, and chelators,
  - pH,
  - Alkalinity/Buffer Capacity,
  - Eh (electrode potential, and



- Groundwater level.

Additionally, peroxide use calls for continuous temperature measurements, and both peroxide and ozone injection call for continuous measurements of oxygen gas, carbon dioxide, and the Lower Explosive Limit (LEL).

### **Contingencies**

The USEPA states that chemical oxidation “may not be technically or economically able to reduce contaminants to background or very low concentrations” (USEPA 2004, page XIII-3). Because chemical oxidation applications are often not successful the first time, “In many cases, multiple application events or extended system operation are required” (ITRC 2005, page 46). Because of the uncertainty of success in using chemical oxidation, the USEPA states that “Contingency plans should also be prepared as part of the remedial design” (USEPA 2004, page XIII-33). These plans should “include response actions to take if performance monitoring data indicate any of the following:

- Inadequate oxidant distribution,
- Inadequate permeation of low permeability soil zones,
- Low petroleum mass reduction rates,
- Excessive contaminant migration,
- Recalcitrance of constituents,
- Production of excessive fugitive emissions,
- Rebound in contaminant levels measured during long term post-application monitoring, or
- Evidence of oxidant moving in wrong direction” (USEPA 2004, page XIII-33).

These are all problems that can and do occur with chemical oxidation applications. No corrective action plan (CAP) should be accepted unless each of these items is completely covered.

### **Safety Issues**

Both liquid and solid peroxides have the same limitations, in that they can not be safely applied to free product, or around piping, tanks, or utility lines. The injections can produce a violently exothermic reaction, particularly in the presence of hydrocarbon free product; producing steam, pressure, and/or an explosive off-gas. PVC wells have also melted during a hydrogen peroxide injection (Huling and Pivetz, 2006). Peroxide use calls for continuous temperature measurements, and both peroxide and ozone injection call for continuous measurements of oxygen gas, carbon dioxide, and the Lower

Explosive Limit (LEL). To prevent problems with off-gassing, the USEPA states, "Special precautions (i.e., SVE [soil vapor extraction] system) are required for appropriate implementation of remedial action involving Fenton's Reagent/hydrogen peroxide" (USEPA 2004, page XIII-3). Sodium permanganate often comes in a liquid solution, at 40% strength. This poses a "significant handling and explosion risk" (USEPA 2004, page XIII-5). Use of a proprietary mix of peroxides and other compounds on a chlorinated pesticide spill in Indiana resulted in the "minor" release of chlorine gas (Holish et al, 2000). The maintenance of on-site ozone generators has resulted in high level ozone exposures for field staff.

### **Indiana Case Studies**

- Hydrogen Peroxide/Fenton's. A major application of hydrogen peroxide was performed in late 2001, at a large industrial site. Low to moderate levels of hydrocarbon contamination were restricted to a small (160 X 100 feet) area near the tank pit. Contamination was also mostly above 10 feet bgs. With this small and fairly isolated area to deal with, IDEM suggested excavation or RISC closure. Instead, the responsible party (RP) elected to use hydrogen peroxide/Fenton's Reagent. The RP addressed most of the safety concerns in a meeting with IDEM, and was given a conditional approval for a trial remediation.

Thirty-six stainless steel injection wells were installed, on 20-foot centers. Each well was 15-feet deep, and screened from 5 to 15-feet. A 3-foot by 3-foot and ½ foot thick concrete pad was built around each well to help prevent breakthrough of the exothermic reaction to the surface. Each well was topped by a wellhead assembly which included intake and exhaust check valves, a pressure gauge, a 14-foot long stringer to extend into the well, and supply piping. The supply hoses were connected to one of the five secondary distribution manifolds, which were connected to the main manifold.

An environmental company, who had extensive experience in hydrogen peroxide applications, performed the injections. First, each well was "conditioned" by the injection of 100 pounds of ferrous sulfate, 2 gallons of hydrochloric acid, and 53 gallons of water. This was intended to produce the iron-rich and acidic conditions needed for Fenton's Reaction to succeed.

Injections were made very slowly, over nearly a month, to help keep pressures down and prevent explosions or breakthrough to the surface. In spite of this, high-pressure breakthroughs near the concrete pads or under the pavement were common, with the chemicals bubbling through to the surface, or even erupting in small (generally less than 2-feet high) geysers. A total of 8,651 gallons of 17.5% hydrogen peroxide solution was injected, along with 162 gallons of conditioner, 159 gallons of acid, and about 1900 gallons of water. This totals 10,872 gallons, for an average of about 300 gallons of liquids for each of the 36 wells.

The site aspects and restricted area of contamination provided optimal conditions for a test of hydrogen peroxide injections for hydrocarbon remediation. The

amount of product injected, and the closely spaced injection points, should have been more than adequate for remediation, if this technique is capable of working effectively in-situ. Although analyses for an in-depth comparison were not provided, the hydrogen peroxide treatments have produced, at best, significantly less than 50% soil cleanup, and a 43% increase in groundwater contamination. The levels of contaminants found in the groundwater have greatly increased, probably due to contaminant mobilization. The groundwater contamination is also spreading, probably due to the more than 10,000 gallons of added liquids.

The injection of hydrogen peroxide was not successful. Although a cost/benefit analysis was not provided, the man-hours and material costs have obviously been high, to obtain worse site conditions than were present before injection. A possible minor soil cleanup is more than offset by a dramatic increase and expansion of groundwater contamination. In all probability, much better results could have been obtained, at less expense, from conventional remediation or RISC closure. The hydrogen peroxide injections have demonstrated a definite lack of remediation effectiveness at this site. Hydrogen peroxide works well in the laboratory and for ex-situ soil or water treatment cells where chemistry can be controlled, but in-situ applications present problems.

- **Ozone.** There are currently several pilot and full-scale ozone systems in Indiana. All are in sandy soil. An ozone micro-sparg system fully remediated the high concentration source area of a petroleum spill in northwest Indiana. Several other petroleum sites are successfully using an ozone sparge enhancement on existing pump and treat and SVE systems. The Office of Land Quality is unaware of any sites in Indiana where ozone is being used to treat chlorinated solvents. More information will be added here as the projects advance.
- **Calcium & Magnesium Peroxide.** IDEM has a fairly extensive file on use of these solid peroxides, and of proprietary blends (mostly of peroxides). There have been some applications in sandy soils that have been fairly successful. To date, The Office of Land Quality has not received validated data showing that site cleanup objectives have been achieved using the solid peroxides in-situ in low-permeable soils. All sites have shown contaminant mobilization, but no cleanup.

Companies claim that they have special catalysts or amendments that allow for successful “non pH dependent Fenton’s Reaction,” or they have a patented delivery system that allows their process to be used even in Indiana’s normally low-permeable zones. These claims have yet to be validated. The actual data from numerous applications has not shown a successful remediation in-situ, in low-permeable soils.

- **Permanganate.** This has been applied at a few sites in Indiana. One site was in fine grained material. It failed because the permanganate could not be distributed (even under high-pressure injection) in the clay. Another was in sand, on low concentrations of chlorinated compounds. It failed as well, probably because the injections could not overcome the NOD of the soil, which was not tested beforehand. Contaminant concentrations did increase, showing some

desorption, but no cleanup. A dry cleaning site in southern Indiana was treated with a 4% permanganate solution, but the contractor injected it at such high volumes (>100 % of the original plume pore volume) that it diluted and expanded the plume. Another contained high levels of TCE, which were treated with large amounts of permanganate. It failed to produce significant remediation, but the reason why was not determined.

- Persulfate. There have been several attempts to use persulfate on chlorinated solvents in various areas of Indiana. One has been successful at pilot scale. At another dry cleaner, the persulfate was actually mixed into the soil with large paddles, but showed no significant remediation. A pilot test in clayey soils at a chemical company was also unsuccessful. The likely cause of the failures is either an insufficient amount of oxidant or the unequal distribution of activator compound with respect to the oxidant.
- RegenOx™. This is a new and emerging product. It has been used successfully on at least one site as a source area treatment in combination with excavation and HRC on the remainder of the plume. IDEM has approved another proposal of RegenOx in combination with AS/SVE, but the work has not yet been implemented.

## **Conclusion**

Chemical oxidation is becoming a widely-used remedial option. However, there are special concerns due to the safety issues, and limitations of this form of remediation. Before a CAP using in-situ chemical oxidation can be approved, it needs to contain:

- 1) A very detailed site characterization, including a precise NAPL delineation, a full preferential pathway assessment, and site-specific hydraulic properties, soil properties, and soil and groundwater chemistry.
- 2) Laboratory results showing the natural oxygen demand (NOD) of the site soils.
- 3) Results of an on-site pilot study, which establishes the oxidant concentrations, injection rates and volumes, temperature, pressures, time of treatment, and radius of influence.
- 4) An SVE system for hydrogen peroxide applications and likely for many ozone injection systems.
- 5) A detailed contingency plan which incorporates the information above.
- 6) A site safety plan, which covers the special problems presented by handling and use of oxidants.
- 7) Plans for site monitoring, with quarterly sampling in the ISCO treatment area, and immediate surroundings, for a minimum of one year.

## **Viability**

The USEPA (2005, page XIII-15), in their section titled 'Overall Viability,' states that there are three "limits of chemical oxidation viability at a site. If review of the corrective action plan indicates that any of the following conditions exist, chemical oxidation is not likely to be a feasible or appropriate remedial solution for the site." These conditions are: the presence of free product, underground utility lines, or low permeable soils.

None of the chemical oxidants can economically remediate free product, and the peroxides can be extremely dangerous if they contact it. Underground utilities can be adversely affected by the heat, VOC vapors, elevated oxygen levels, and potential corrosion that can occur with chemical oxidation treatments. The problems of low permeable soils may be helped by soil fracturing, using the less reactive oxidants, or repeated treatments. However, none of these are guaranteed to work, and all this adds to the expense and time needed.

In sum, if low permeable soil is encountered, chemical oxidation should not be a first choice for remediation. If a contractor or site owner is insistent upon using oxidants in a silty or clay zone, the preceding CAP requirements are needed, plus a contingency for alternative remediation if ISCO fails.

## **Recommendations**

The information available at this time does not support using chemical oxidants for most in-situ applications in low permeable soil. The solid peroxides may be useful in sandy soil, on low levels of contamination. Ozone treatment seems to be useful, on some sites. Because of the safety issues, The Office of Land Quality recommends disapproval of any corrective action plan using liquid hydrogen peroxides in-situ without an aggressive vapor and groundwater capture system.

Due to the extreme variability in results from ISCO systems, and the long list of things the USEPA states can go wrong with ISCO treatments (above), all chemical oxidation treatments should be on a pay-for-performance basis for any State funded cleanup.

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### **Further Information**

If you have any additional information regarding this technology or any questions about the evaluation, please contact Bob Sonnefeld, Senior Geologist, at (317) 234-4688 or by e-mail at [rsonnefi@idem.IN.gov](mailto:rsonnefi@idem.IN.gov). You may also contact Sarah Finley-Johanson, Geologist, at (317) 234-0997 or by e-mail at [sfinley@idem.IN.gov](mailto:sfinley@idem.IN.gov). This technical guidance document will be updated periodically or as new information is acquired.